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CARDIFF (WALES) R H WILLIAMS 01 APR 87
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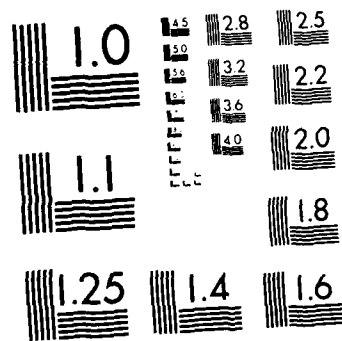
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METAL CONTACTS ON SEMICONDUCTORS

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Principal Investigator: Professor R.H. Williams
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Experiments involving metal contacts on a number of semiconductors have continued during the last six months. Microscopic interactions of a range of metals with clean and oxidised indium phosphide surfaces have been investigated by soft X-ray photoemission and a substantial effort has been directed towards the interpretation of the data obtained. We have concentrated, in particular, on the transition metals ^{Cr, Mn and V} Cr, Mn and V, and also on the alkali metal Na. The transition metals are all highly reactive with clean InP, and give a range of Schottky barriers between ohmic and 0.4 eV. We have also investigated Schottky barriers for thick films of these metals deposited on clean cleaved (110) InP surfaces, by I-V and C-V techniques. This complete work is now being prepared for publication. Papers on these investigations were present at the UK Annual Solid State Physics Conference, in December 1986.

Indium Phosphide M.J.M.

A substantial effort has been directed into a study of Sb contacts on clean InP(110) surfaces. Antimony is a particularly interesting case. When deposited on clean GaAs (110) surfaces it yields a Schottky barrier height comparable with those for metals such as Al, Ni, Ag and Au. The behaviour on n-InP (110) surfaces, however, is entirely different. For ultra thin layers, a barrier height of around 0.4 eV is obtained, but for layers thicker than around 8 Å the contact becomes highly ohmic. Raman spectroscopy has been used to investigate this contact and the results indicate a barrier height of less than 0.1 eV for a thick Sb contact on n-InP(110) clean surfaces. These studies are now being extended to p-InP and our I-V and C-V studies demonstrate a Schottky barrier height with a value close to the band gap. This is entirely consistent with the data on n-type crystals. It is hard to see how these data can be understood in

(1)

terms of the metal-induced-gap-states model of Schottky barrier formation. It is easier to see that a defect model might be more applicable. Deposition of thin layers of Sb leads to a strained layer, which becomes an unstrained crystalline layer for coverages in excess of 8 Å. At the same time defects may be generated at the interface giving rise to the ohmic behaviour on n-type crystals. This data is now being fully analysed for publication.

From the above studies, and others carried out by our group, it is quite clear that Schottky barriers on n-InP cover a large range between 0.1 eV and 0.6 eV. This is in sharp contrast to the recent claims that these barriers all lie between 0.3 eV and 0.5 eV. It has also been claimed recently that oxide layers do not influence Schottky barriers at metal-InP interfaces, contrary to the findings of our group several years ago. We have now checked this further and confirmed our earlier conclusions, namely that intermediate oxide layers at metal-InP interfaces have a drastic effect on Schottky barrier heights. This work will also be published when complete.

These studies are now being extended to the II-VI semiconductor CdS. Raman spectroscopy is being used to probe band bending at barrier interfaces, I-V and C-V methods to study thick film barrier heights, and surface science techniques to study microscopic interactions. We are concentrating on CdS because of its particular relevance in the context of the much debated covalent-ionic transition, if it exists.

As part of this project, a study of the heterojunction interface between InSb and CdTe has also been carried out using Raman spectroscopy. This interface is a particularly interesting one in possible devices for infra

red detection and application of soft XPS techniques by us demonstrated that interfaces prepared under MBE conditions are not atomically abrupt. In this study we were able to demonstrate that the compound formed at the interface is most probably In_2Te_3 . This was achieved by growing In_2Te_3 crystals and measuring Raman spectra from them. These were compared with Raman spectra for InSb-CdTe interfaces prepared at room temperature and prepared under MBE conditions. This work has now been accepted for publication and preprints are enclosed.

The formation of interfacial layers in InSb-CdTe heterostructures studied by Raman scattering

D.R.T. Zahn, K.J. Mackey, R.M. Williams

Department of Physics, P.O. Box 78, University College
Cardiff CF1 1XL, UK

H. Mündler, J. Geurts and W. Richter

1. Physikalisches Institut der RWTH Aachen, Sommerfeldstr. 28
D-5100 Aachen, FRG

Abstract

The formation of a thin interfacial layer of indium telluride in InSb-CdTe heterostructures has been previously suggested by photoemission (PES) results. However, the detailed nature of this layer was difficult to interpret by PES. Therefore samples being previously investigated by PES were studied by Raman spectroscopy. Spectra were taken of heterostructures grown by deposition of CdTe on (100)InSb substrates at room and elevated temperatures. For the room temperature sample the vibrational modes of CdTe and crystalline Te were detected. In the case of elevated substrate temperatures it was possible to identify the interfacial layer rich in indium and tellurium as consisting of In_2Te_3 using the Raman spectrum of In_2Te_3 as a fingerprint. Furthermore, the segregation of antimony was confirmed by the detection of the vibrational modes of antimony at the interface.

InSb-CdTe heterostructures are the subject of active current research by many groups /1,2,3,4/. This system is perfectly lattice matched ($\Delta a/a < 0.05\%$) and the combination of a large band gap (CdTe 1.45 eV) with a small band gap material (InSb 0.18 eV) makes it a promising system for the investigation of quantisation effects and the application of multiquantum well lasers and detectors. Critical to the operation of any such device is the quality and stability of its interface. Recent investigations however, have shown that CdTe polycrystallites and Te precipitates were formed when CdTe was deposited on InSb at substrate temperatures below 150°C . /5/. In the temperature range between 150° and 300°C well ordered overlayers were achieved /1/, although the interface between the single crystal CdTe and the InSb substrate was not abrupt as judged by PES results /6,7/. An interfacial layer rich in indium and tellurium was found to be formed. It was suggested that a substantial component of this layer might be In_2Te_3 .

In this communication we describe Raman spectroscopy studies on the interface layer at InSb-CdTe boundaries. In addition InSb and In_2Te_3 crystals have been investigated in an attempt to identify the interface phases formed.

The heterostructures were prepared by depositing CdTe from a single source onto clean and ordered $c(2 \times 8)$ (100)InSb surfaces held both at room and elevated temperature ($T=220^\circ\text{C}$). Full details of the preparation can be found elsewhere /6,7/. The In_2Te_3 sample was grown by horizontal Bridgman method in our laboratory and the structure was confirmed by X-ray diffraction. Samples prepared at both temperatures together with InSb substrate and In_2Te_3 crystals were mounted side by side on a coldfinger in a cryostat and cooled to liquid nitrogen temperature.

Spectra were taken in back scattering geometry using an Ar^+ ion laser ($\lambda=514.4 \text{ nm}$) as a light source and a conventional Spex double monochromator system to detect scattered light. The incident and scattered light were polarized along a (110) direction of the substrate and heterostructure samples. For this scattering geometry symmetry selection rules allow InSb-LO phonon scattering from the (100) surface, whereas InSb-TO phonon scattering is forbidden. Since the In_2Te_3 sample was not single crystal throughout, the geometry was not well known and therefore the scattered light was not polarized. The incident laser power was kept below 40 mW.

Raman spectra for the three samples investigated are shown in figure 1. Spectrum (a) is for clean InSb, spectrum (b) for CdTe deposited onto room temperature InSb substrates, and (c) onto substrates at elevated temperatures.

The substrate spectrum shows the InSb LO phonon line at 193 cm^{-1} . A shoulder exists on its low frequency side. This is due to the normally forbidden TO phonon scattering. The intensity and halfwidth of this feature is known to be dependent on sample quality. A slight deviation from backscattering geometry also contributes to TO phonon scattering. In order to enhance weak features in the heterostructure spectra this substrate spectrum was subtracted from both others ((b) and (c)). The results are shown for samples prepared at room and elevated temperatures in figures 2 ((b)-(a)) and 3 ((c)-(a)) respectively.

Consider first the heterostructure formed at room temperature. The negative values arise from attenuation of the InSb phonon scattering in the CdTe overlayer (approximately 100 monolayers deposited). The positive tail at the low frequency side of the spectrum is caused by an increase in elastic

scattering when CdTe is deposited. This is consistent with increased roughness caused by polycrystalline growth. The most relevant features occur between 120 and 175 cm^{-1} where several peaks overlap and assignment is made difficult except for two peaks at 128 cm^{-1} and 168 cm^{-1} . The peak at 168 cm^{-1} corresponds to the CdTe LO phonon frequency. The other at 128 cm^{-1} is due to scattering by the A1 mode of tellurium. The existence of elemental Te probably as precipitates has been reported by other workers /5/. The A1 mode however, is shifted by an amount equal to 7 cm^{-1} compared to the bulk value of 121 cm^{-1} /8/. This can be explained in terms of tensile stress at the interfacial precipitates of Te. The same shift has been observed for chemomechanical polished or etched surfaces of CdTe where a residual layer of polycrystalline Te of thickness of some 10-40 Å was found to be formed /9/. Unfortunately the E' mode of Te and the CdTe TO phonon have similar frequencies which lead to the observed broadened feature as a result of the overlapping peaks.

Consider now the CdTe deposited on to the InSb substrate at elevated temperature. In this case the equivalent of about 20 monolayers of CdTe was deposited (estimated using a quartz crystal thickness monitor). Photoemission studies were performed on this sample at various stages during growth. In the initial stages an increasing Te^{4d} core level emission signal together with a decreasing Sb^{4d} signal was observed. However, the In^{4d} signal decreased only slowly and Cd could not be detected. It was therefore suggested that a layer rich in indium and tellurium rather than CdTe was formed. At the onset of Cd adsorption (approximately 20 monolayers) growth was interrupted in order to investigate this interfacial layer further using Raman spectroscopy.

Comparison of figure 3 with figure 2 the difference between both samples

becomes obvious. Consistent with the photoemission studies there is no evidence of the CdTe LO phonon. There is also no sign of elemental Te. Due to the thinner overlayer deposited attenuation for this sample is much smaller. However, in figure 3 several salient features occur which will be explained shortly.

A literature survey failed to reveal Raman data of In_2Te_3 , whereas data were available for InTe /10/. In order to identify the interfacial layer Raman spectra of In_2Te_3 crystals were taken. A typical example of which is shown in figure 4. The main features are labelled A', B', C' and D'. Similar features (labelled A, B, C and D) are seen in figure 3 indicating the presence of In Te whereas the Raman spectrum of InTe appears to be entirely different. The relative peak positions and heights especially for the peaks A, B and C are almost identical. The D peak, however, overlaps with the InSb features and its height is therefore not comparable. All four peaks are shifted by the same amount which again can be introduced by stress in such a thin layer (the lattice mismatch between InSb and In_2Te_3 is approximately 5%). There is also evidence for the presence of small features overlapping the elastic tail in figure 3. These probably correspond to the features which can be seen at low frequency in figure 4. We conclude that by comparison of figures 3 and 4 there is strong evidence for the presence of In_2Te_3 at the interface.

The problem now remains of what has happened to the antimony following the formation of this In_2Te_3 layer. The answer is apparent from figure 3 where the existence of polycrystalline Sb is confirmed by the presence of the Al_g mode of Sb at 155 cm^{-1} . This supports the previous suggestion based on a chemical shift of the Sb^{4d} core level that Sb is liberated by the strong chemical reaction at the interface /7/. As shown earlier /11,12/ such a

layer of Sb can be detected when InSb is oxidized at temperatures above 200°C where the formation of In oxide leads to an excess of Sb.

The chemical and structural nature of the interface at InSb-CdTe heterostructures strongly depends on the temperature during the deposition of CdTe. At room temperature crystalline CdTe as well as Te are observed by their vibrational modes. The detection of In_2Te_3 and Sb modes for elevated temperature deposition confirms earlier suggestions that the interfacial layer rich in indium and tellurium is largely In_2Te_3 and that the reaction leads to the liberation of antimony [6,7]. The data described above again illustrate the ability of Raman spectroscopy to provide useful complementary information in surface science.

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Figure Captions

Fig.1:

Raman spectra ($\lambda = 514.5 \text{ nm}$, $T = 80\text{K}$) of

(a) (100)InSb substrate

(b) CdTe deposited on (100)InSb at room temperature (100 ML)

(c) CdTe deposited on (100)InSb at elevated temperature (220°C , 20 ML)

Fig.2:

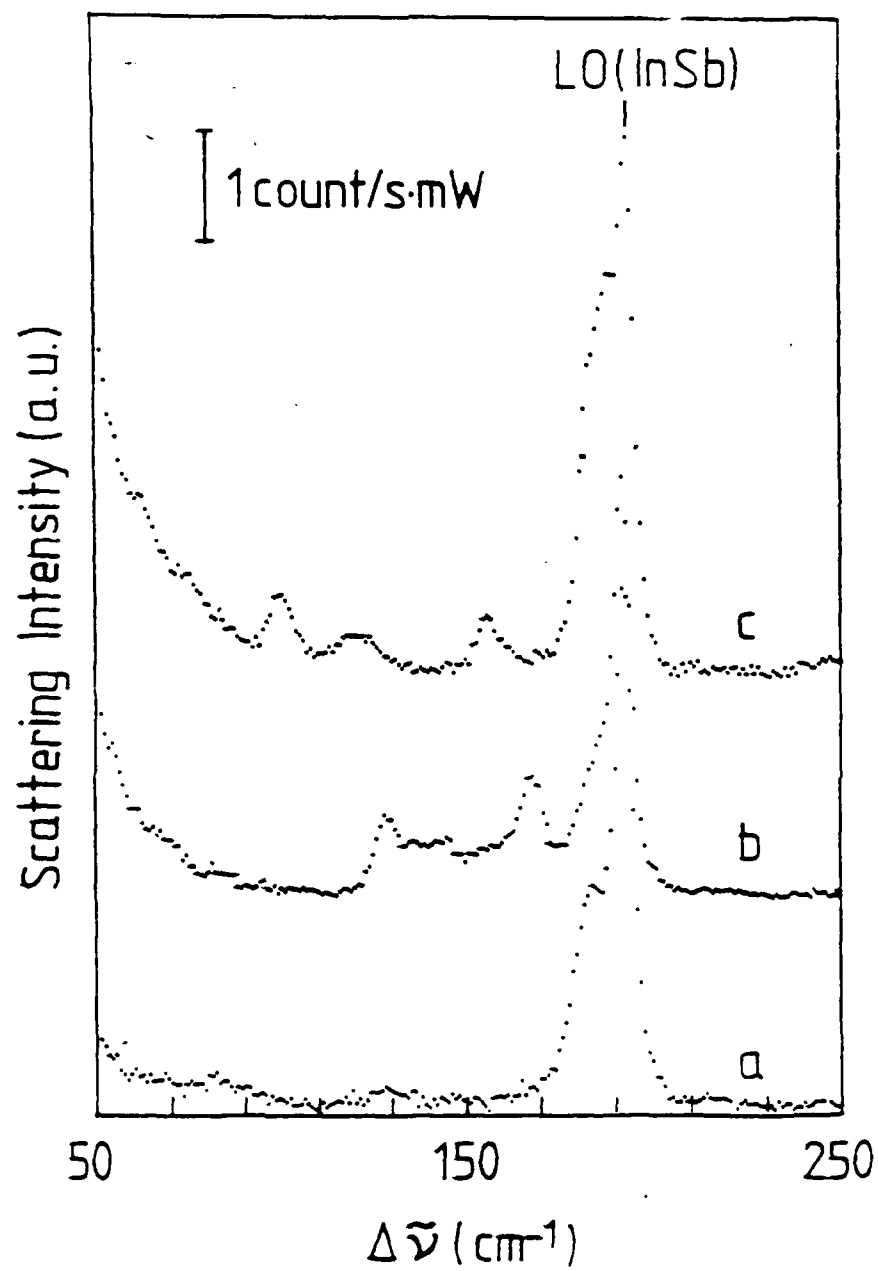
Difference spectrum (b)-(a) of fig. 1 giving the contribution of the overlayer deposited at room temperature

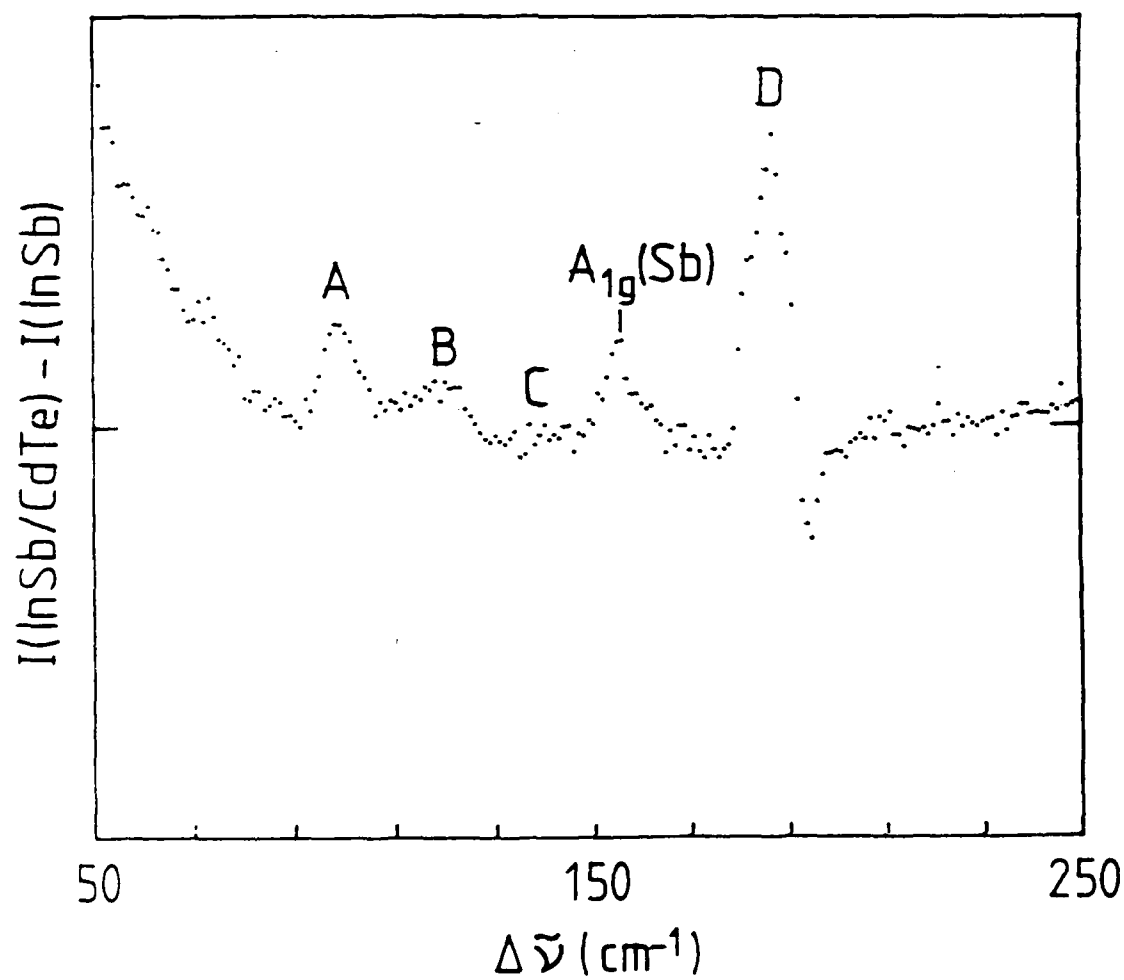
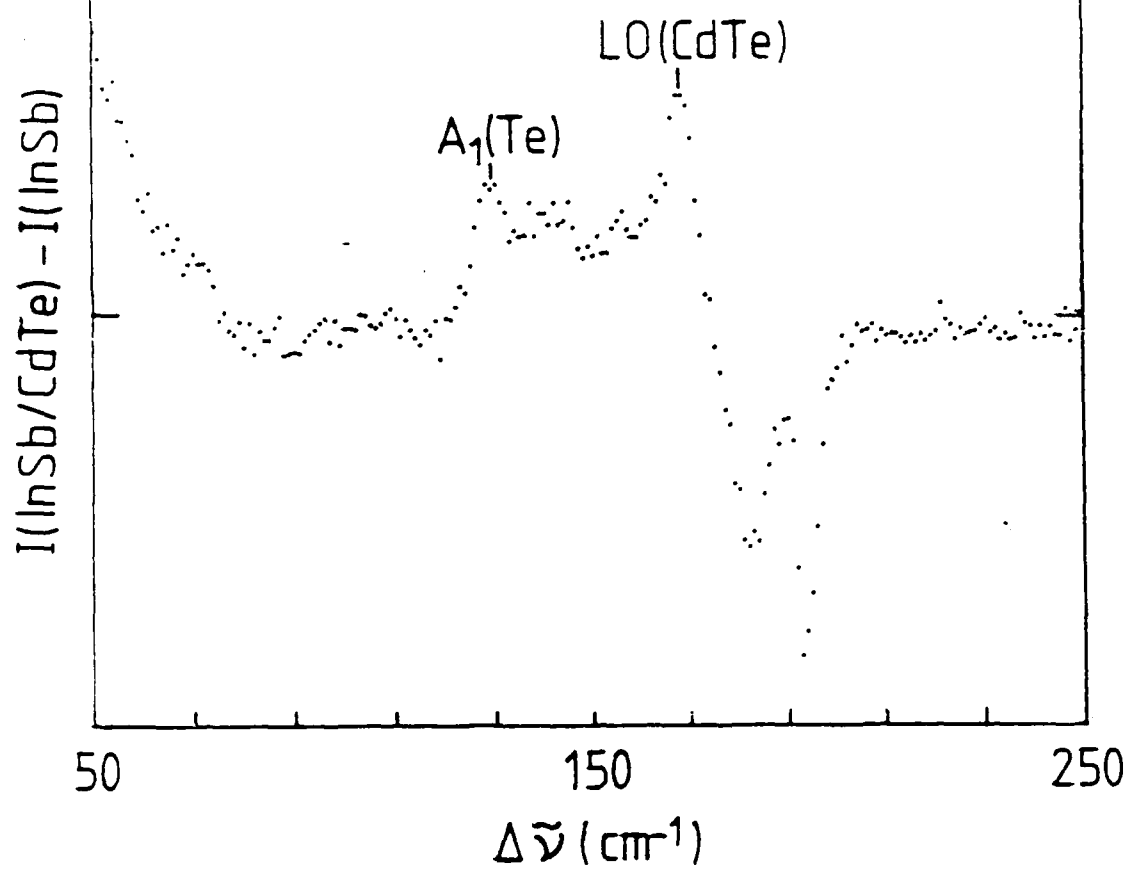
Fig.3:

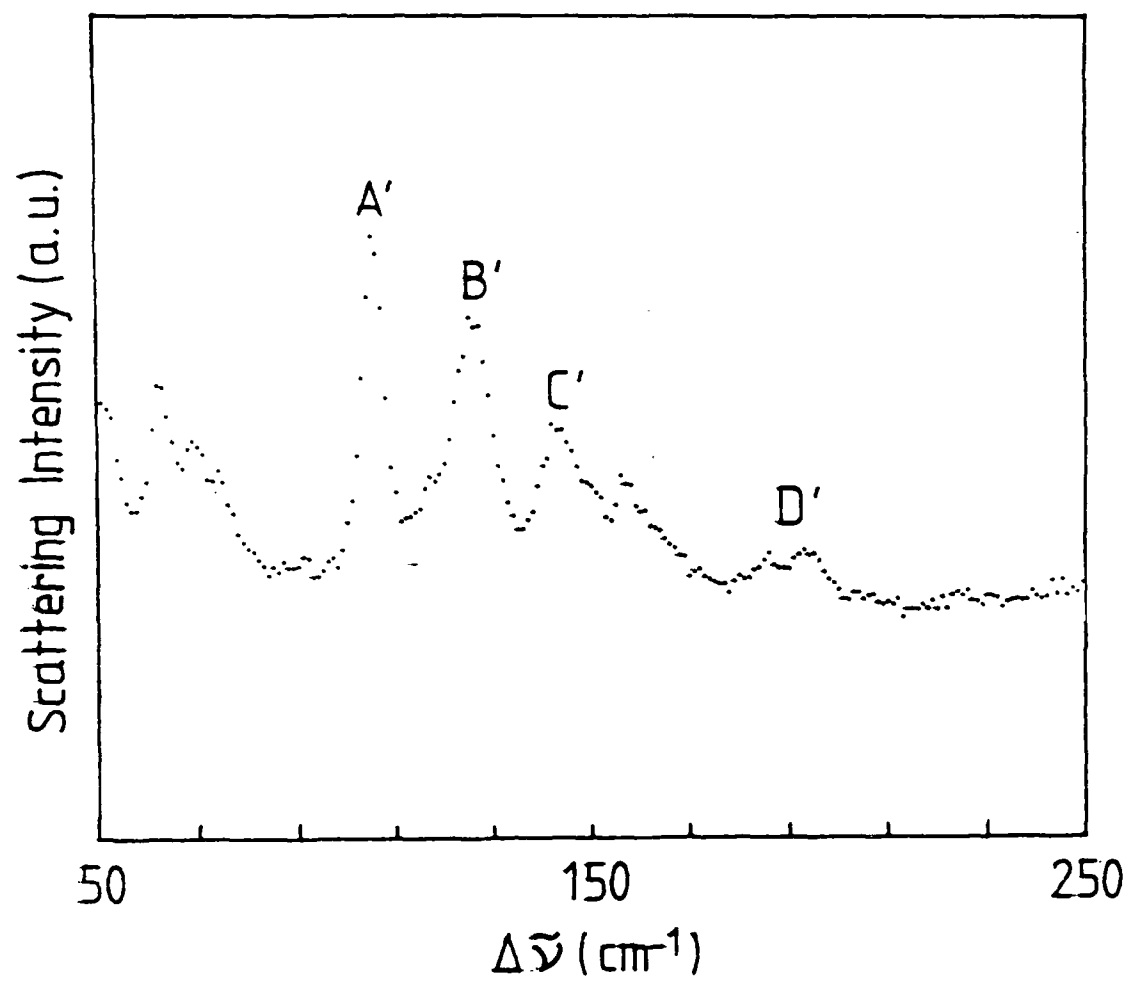
Difference spectrum (c)-(a) of fig.1 giving the contribution of the overlayer deposited at elevated temperature

Fig.4:

Raman spectrum of In_2Te_3 ($\lambda = 514.5 \text{ nm}$, $T = 80\text{K}$)







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